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**(54) [Title of the Invention] METHOD FOR MANUFACTURE OF POSITIVE ELECTRODE ACTIVE MATERIAL FOR ALKALINE BATTERY**

**(57) [Abstract]**

[Task] To provide a method for the manufacture of a positive electrode active material for an alkaline battery that has excellent discharge capacity and charge-discharge cycle characteristic.

[means] The method for the manufacture of a positive electrode active material for an alkaline battery in accordance with the present invention comprises a step of conducting treatment of nickel hydroxide with a cobalt content of less than 90 mol% (Co/(Ni + Co)), ozone and/or oxygen in an alkaline solution.

[Patent Claims] A method for the manufacture of a positive electrode active material for an alkaline battery comprising a step of processing nickel hydroxide with a cobalt content ratio of less than 90 mol% (Co/(Ni + Co)) and ozone and/or oxygen in an alkaline solution.

**[Detailed Description of the Invention]**

[Field of Technology] The present invention relates to the improvement of manufacturing conditions in a method for the manufacture of a positive electrode active material for an alkaline battery.

[0002]

[Prior Art Technology] Nickel oxyhydroxide has been used as a positive electrode active material in nickel-cadmium storage batteries, nickel-zinc storage batteries, and nickel-hydrogen storage batteries. Usually when such batteries are manufactured, an active material in a discharged state is used together with a positive electrode plate and a negative electrode plate. Thus, nickel hydroxide is used for a positive electrode and cadmium hydroxide, zinc oxide, a hydrogen storage alloy, or a hydrogen storage metal is used for a negative electrode. On the other hand, the battery can be also fabricated with the active material in the charged state, that is, nickel oxyhydroxide is used for the positive electrode and metallic cadmium, metallic zinc, or a hydrogen absorbing alloy or hydrogen absorbing metal that has absorbed hydrogen is used for the negative electrode.

[0003] A method for synthesizing nickel oxyhydroxide was described in JP-A-6-31045 and Z. An Org. Chem., 261, 26, 1950. With this method a compound of nickel with a valence of two, such as nickel hydroxide, nickel nitrate, nickel sulfate, or  $K_2[(CN)_4]$  is chemically oxidized in an aqueous alkaline solution by using a strong oxidizing agent such as potassium peroxodisulfate-sodium perchlorate. However, with this method, the type and composition of the reaction product vary significantly depending on the reaction temperature and physical properties of starting material and nickel oxyhydroxide with high purity is difficult to obtain with good stability. Therefore, lithium nickel oxide using the nickel oxyhydroxide obtained by this method as a starting material is difficult to obtain with a high purity due to the presence of impurities contained in the nickel oxyhydroxide. This is one of the main reasons for the degradation of properties of positive electrode active material for lithium batteries. Further, in the same references, an attempt was made to synthesize nickel oxyhydroxide by electrochemical oxidation employing nickel hydroxide as a starting material. However, because the electron conductivity of nickel hydroxide is very low ( $10^{-12}$ - $10^{-14}$  S·cm<sup>-1</sup>), it is necessary to introduce into an electrode material an electrically conductive additive, such as graphite or a metal powder, that can increase the electron conductivity of the electrode material.

[0004]

[Problems Addressed by the Invention] Nickel oxyhydroxide is used as a positive electrode active material for alkaline secondary batteries such as nickel-cadmium storage batteries, nickel-zinc storage batteries, or nickel-hydrogen storage batteries, but the reaction conditions of chemical synthesis methods thereof are extremely severe, as described hereinabove, and a manufacturing process capable of providing products with good stability is difficult to implement. In order to resolve this problem, it is necessary to optimize the reaction conditions such as physical properties of starting materials, reaction temperature, and synthesis procedure.

[0005] However, useful reaction conditions have not yet been established. Furthermore, if peroxodisulfate is used as an oxidizing agent after the completion of synthesis reaction, then the reaction produces a sulfate ion as an impurity and this impurity is difficult to remove. When this impurity is present even in a very small amount in nickel oxyhydroxide, it causes significant degradation of properties thereof as a battery active material. Therefore, it becomes necessary to use an oxidizing agent that does not generate such an impurity.

[0006] The method for the manufacture of a positive electrode active material for an alkaline battery in accordance with the present invention comprises a step of processing nickel hydroxide with a cobalt content ratio of less than 90 mol% ( $\text{Co}/(\text{Ni} + \text{Co})$ ) and ozone and/or oxygen in an alkaline solution. As a result, nickel oxyhydroxide which contains no impurities and is a high-purity positive electrode active material for alkaline batteries can be obtained.

[0007]

[Description of the Preferred Embodiments] The present invention relates to the improvement of manufacturing conditions in a method for the manufacture of a positive electrode active material for an alkaline battery, this method comprising a step of processing nickel hydroxide with a cobalt content ratio of less than 90 mol% ( $\text{Co}/(\text{Ni} + \text{Co})$ ) and ozone and/or oxygen in an alkaline solution and being suitable for nickel-cadmium storage batteries, nickel-zinc storage batteries, or nickel-hydrogen storage batteries.

[0008] The nickel oxyhydroxide obtained by this method contains no impurities and has a high purity. Therefore, an alkaline battery can be obtained which has excellent discharge capacity and charge-discharge cycle characteristic.

[0009] The present invention will be described below based on the preferred embodiments thereof.

[0010] [Embodiment 1] A mixed gas (mixed gas of oxygen + ozone) containing 10% ozone obtained with a discharge ozonizer was passed, under stirring, for 8 h at a rate of  $0.2 \text{ dm}^3/\text{min}$  through 2 L of 4.5 M aqueous sodium hydroxide solution having 100 g of nickel hydroxide powder with a particle size 5-50  $\mu\text{m}$  dispersed therein. Then, the powder was washed and dried for 2 h at a temperature of  $80^\circ\text{C}$  to obtain nickel oxyhydroxide A for a positive electrode active material of an alkaline battery in accordance with the present invention.

[0011] [Embodiment 2] A total of 100 g of nickel oxyhydroxide powder with a particle size of 5-50  $\mu\text{m}$  and a cobalt content of  $\text{Co}/(\text{Ni} + \text{Co}) = 15 \text{ mol\%}$  was added to 2 L of a 4.5 M aqueous solution of potassium hydroxide held at a temperature of  $60^\circ\text{C}$ . A mixed gas (mixed gas of oxygen + ozone) containing 20% ozone obtained by electrolysis of a sulfuric acid solution with a specific gravity of 1.2 with by using platinum electrodes was passed through the liquid under stirring, for 5 h at a rate of  $0.3 \text{ dm}^3/\text{min}$ . Then, the powder was washed and dried for 2 h at a temperature of  $80^\circ\text{C}$  to obtain nickel oxyhydroxide B for a positive electrode active material of an alkaline battery in accordance with the present invention.

[0012] [Comparative study] FIG. 1 shows the powder X ray diffraction patterns ( $\text{CuK}\alpha$ ) of nickel oxyhydroxide used as a positive electrode active material for an alkali battery in accordance with the present invention, that was obtained in Embodiments 1 and 2 and nickel hydroxide as a starting material therefor. The conditions for the X ray diffraction were as follows: output voltage 50 kV, output current 200 mA, and scan speed  $4^\circ/\text{min}$ .

[0013] Further, (a) relates to nickel hydroxide which is a starting material , and (b) and (c) relates to nickel oxyhydroxide prepared in Embodiments 1 and 2, respectively.

[0014] For comparison, figure (d) shows an X ray diffraction pattern of the product C prepared in the same manner as in Embodiment 1, except that no ozone was used and treatment was conducted with sodium peroxodisulfate.

[0015] Data shown in the figures demonstrate that in the case of (d), the unreacted nickel hydroxide remained in addition to the nickel oxyhydroxide, which is the target product, and the reaction yield was low. This can apparently be explained by the fact that the oxidation reaction of alkaline aqueous solution induced by the peroxodisulfate used as an oxidizing agent proceeded as a side reaction and inhibited the main reaction.

[0016] Then, the quantity of alkali metal cations contained in nickel oxyhydroxide obtained in the cases (b), (c), and (d) was measured by ion chromatography.

[0017] The results obtained showed that practically no alkali metal cations were observed in the nickel oxyhydroxide (b) and (c) in accordance with the present invention, but in (d), the presence of sodium ions as impurities was confirmed. Because all the samples of nickel oxyhydroxide obtained were washed under the same conditions, this result can be apparently attributed to the fixation of sodium ions in the crystal structure.

[0018] When the product is used as an active material for a battery or as a starting material for the active material for a battery, this impurity blocks the diffusion channels for lithium ions or hydrogen ions, causing degradation of electrochemical properties. Therefore, it is highly desirable that a high-purity  $\beta$ -nickel oxyhydroxide containing no such impurities be used as the battery active material.

[0019] Both the nickel oxyhydroxide (b) and the nickel oxyhydroxide (c) for a positive electrode active material of an alkali battery in accordance with the present invention are high-purity nickel oxyhydroxide and a battery with excellent electrochemical characteristics can be fabricated.

[0020] [Battery Evaluation Test] Alkali batteries were fabricated in the manner as follows. A positive electrode plate with a size of 25 mm x 25 mm was fabricated by using the nickel oxyhydroxide obtained in Embodiments 1 and 2 as a positive electrode active material, admixing 5 wt.% metallic nickel as an electrically conductive additive and 5 wt.% CMC as a binder, adding water to obtain a paste, coating the paste on a nickel mesh serving as a collector and drying at a temperature of 100°C.

[0021] A test battery was fabricated by using this positive electrode plate 1, a metallic nickel plate 2 of the same size as a counter electrode, and 300 mL of 5M aqueous solution of potassium hydroxide as an electrolytic solution. A mercury/mercury oxide reference electrode was used for measuring the potential of the positive electrode.

[0022] The batteries were charged for 16 h at a current density (10 hr ratio) of 3.0 mA/cm<sup>2</sup> and a temperature of 25°C, and then discharge was conducted to 0 V at the same current density.

[0023] The discharge characteristics of the nickel oxyhydroxide A and B in accordance with the present invention are shown in FIG. 2. The results relating to the conventional positive electrode C manufactured by the same method by using the nickel oxyhydroxide having the X ray diffraction pattern shown in FIG. 1(d) were used as the conventional example for comparison.

[0024] [Evaluation Results] The comparison of discharge capacity of positive electrode plates shown in FIG. 2 demonstrates that the active material obtained by the conventional method has a capacity of about 250 mAh/g, whereas the active material in accordance with the present invention has a capacity of about 290 mAh/g. In other words, the positive electrode plate comprising the nickel oxyhydroxide in accordance with the present invention has superior electrochemical properties. Further, a charge-discharge cycle test was conducted for all the batteries under the same conditions and the capacity retention ratio in the 300-th cycle with respect to the initial capacity was compared for the batteries. The results were as follows: A – 80%, B – 90%, C – 60%. Therefore, the batteries using the nickel oxyhydroxide in accordance with the present invention demonstrated excellent cyclic characteristic.

[0025]

[Effect of the Invention] The present invention relates to the improvement of manufacturing conditions of a method for the manufacture of nickel oxyhydroxide positive electrode active material for an alkali battery that is suitable for nickel-cadmium storage batteries, nickel-zinc storage batteries, and nickel-zinc storage batteries. The improved method is characterized in that it comprises a step of conducting treatment in an alkaline solution of nickel hydroxide with a cobalt content of less than 90 mol% ( $\text{Co}/(\text{Ni} + \text{Co})$ ), ozone and/or oxygen.

[0026] The nickel oxyhydroxide obtained by the above-described method contains no impurities and has a high purity. Therefore, an alkali battery with excellent discharge capacity and charge-discharge cycle characteristic can be provided.

[0027] The nickel oxyhydroxide for a positive electrode active material of an alkaline battery in accordance with the present invention is a high-purity  $\beta$ -nickel oxyhydroxide comprising no phase in which an alkali metal such as sodium is fixed between the layers of  $\text{NiO}_6$  in the crystal structure. As a result, when this nickel oxyhydroxide is used as an active material for an alkaline battery, because it contains practically no impurities, excellent electrochemical characteristic with a very small decrease in capacity in charge-discharge cycles can be obtained.

[0028] Accordingly, the present invention has a high industrial value.

[Brief Description of the Drawings]

FIG. 1 is an Z ray diffraction pattern.

FIG. 2 shows a discharge characteristic of the positive electrode plates A, B in accordance with the present invention and positive electrode C obtained by the conventional method.

FIG.. 1

FIG. 2

Ordinate: potential

Abscissa: discharge capacity